

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

Chinese Patent No. 1352203 A

---

Job No.: 6194-94964

Translated from Chinese by the Ralph McElroy Translation Company  
910 West Avenue, Austin, Texas 78701 USA

PEOPLE'S REPUBLIC OF CHINA  
 NATIONAL OFFICE OF INTELLECTUAL PROPERTY  
 INVENTION AND PATENT APPLICATION JOURNAL  
 PATENT NO. CN 1352203A

Int. Cl. <sup>7</sup> :	C08F 10/00 C08F 4/42
Filing No.:	01140470.1
Filing Date:	December 10, 2001
Publication Date:	June 5, 2002
Number of pages of claims:	4
Number of pages of description:	14
Number of pages of attached figures:	0

POLYMERIZED "POST-MAO"  $\alpha$ -DIIMIDE NICKEL CATALYST FOR  
 POLYMERIZATION OF OLEFINS

Inventors:	Guo-xin Jin Dao Zhang
Applicant:	Chinese Academy of Science Applied Chemistry Research Institute  Gui-Zhen Cao 159 Ren-min Da Dao Chang-chun City, Jilin Province 130022

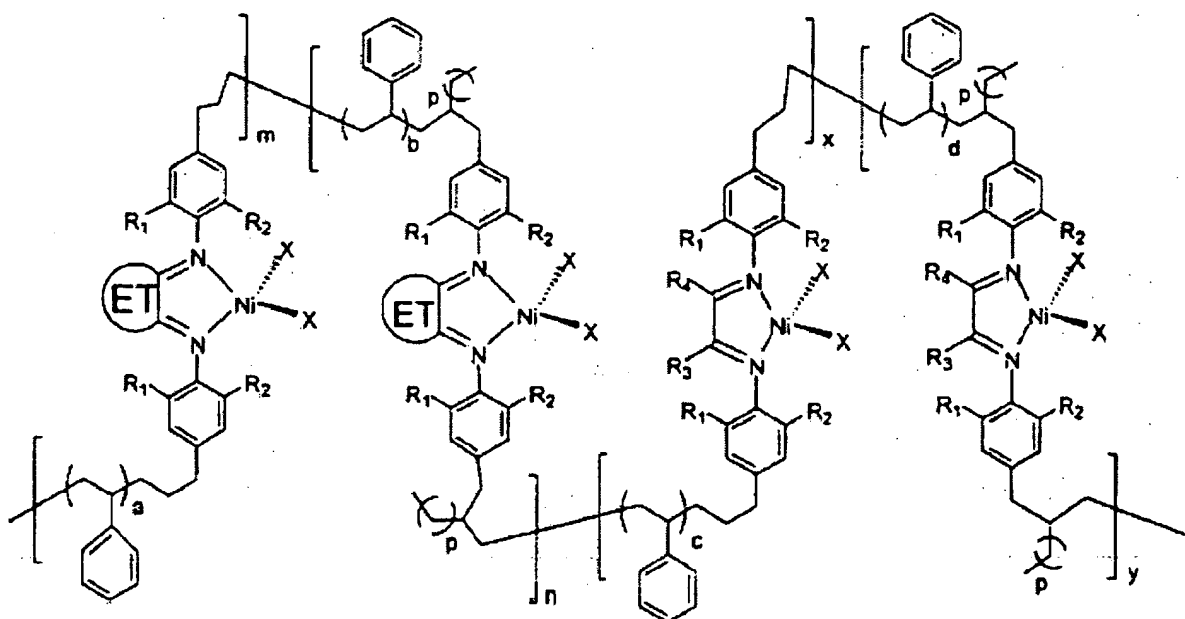
Abstract

This invention pertains to the preparation of polymerized "post-MAO"  $\alpha$ -diimide nickel catalysts for the polymerization of olefins and the polymerization of ethylene catalyzed by such. The catalysts consist of components A and B, in that component A is expressed by formula [P(S-co-Cat)] or SiO<sub>2</sub>-P(S-co-Cat)], where P represents a copolymer, S is polystyrene, co represents copolymerization and Cat represents 1-4 kinds of "post-MAO"  $\alpha$ -diimide nickel

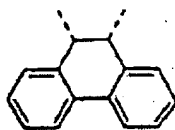
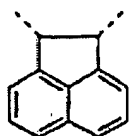
catalysts containing alkenyl groups. [P(S-co-Cat)] are coordination compounds formed by 1-4 kinds of neutral ligands for  $\alpha$ -diimide with nickel, in that the positions para to the amino group contain alkenyl groups that copolymerize with styrene to form polymerized "post-MAO" catalysts for olefin polymerization.  $\text{SiO}_2$  represents a silicon dioxide carrier that immobilizes polymerized  $\alpha$ -diimide nickel catalysts [P(S-co-Cat)]. Component B is methylaluminoxane and boron pentafluorobromobenzene  $[\text{B}(\text{C}_6\text{F}_5)_3]$ . This type of catalyst for catalyzing ethylene polymerization possesses a high activity and is suitable for gas phase and slurry polymerization processes and the polymer products contain no inorganic ash.

### Claims

1. A polymerized "post-MAO"  $\alpha$ -diimide nickel catalyst for olefin polymerization comprising components A and B, in that component A is expressed by formula [P(S-co-Cat)] or  $\text{SiO}_2\text{-P(S-co-Cat)}$ , where P represents a copolymer, S is polystyrene, co represents copolymerization, Cat represents 1-4 kinds of "post-MAO"  $\alpha$ -diimide nickel catalysts containing alkenyl groups; [P(S-co-Cat)] are copolymers of 1-4 kinds of  $\alpha$ -diimide nickel catalysts and styrene, having the following structure:

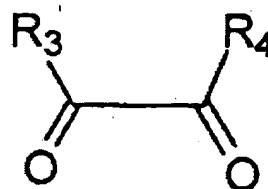
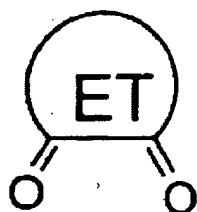


where M represents Ni; x is Cl or Br; p is an integer of 0-4; a, b, c, d, m, n, x and y are integers of 0-150  $R_1$  and  $R_2$  may be the same or different and represent H, methyl groups, isopropyl groups or tert-butyl groups  $R_3$  and  $R_4$  may be the same or different and represent methyl groups, ethyl groups, propyl groups or heterocyclic groups and ET is selected from the following divalent residues of cyclic compounds or mixtures thereof:

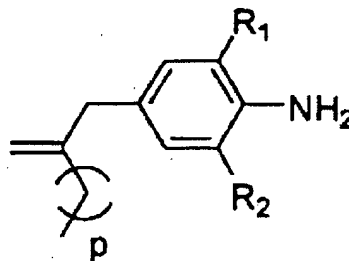
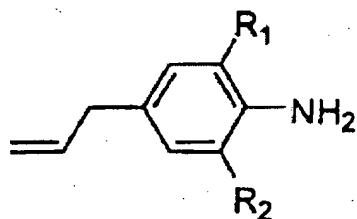


$\text{SiO}_2$  represents a silicon dioxide carrier immobilizing polymerized catalyst  $[\text{P}(\text{S-co-Cat})]$ ; component B is selected from methylaluminoxane and pentafluorobromobenzene  $[\text{B}(\text{C}_6\text{F}_5)_3]$ .

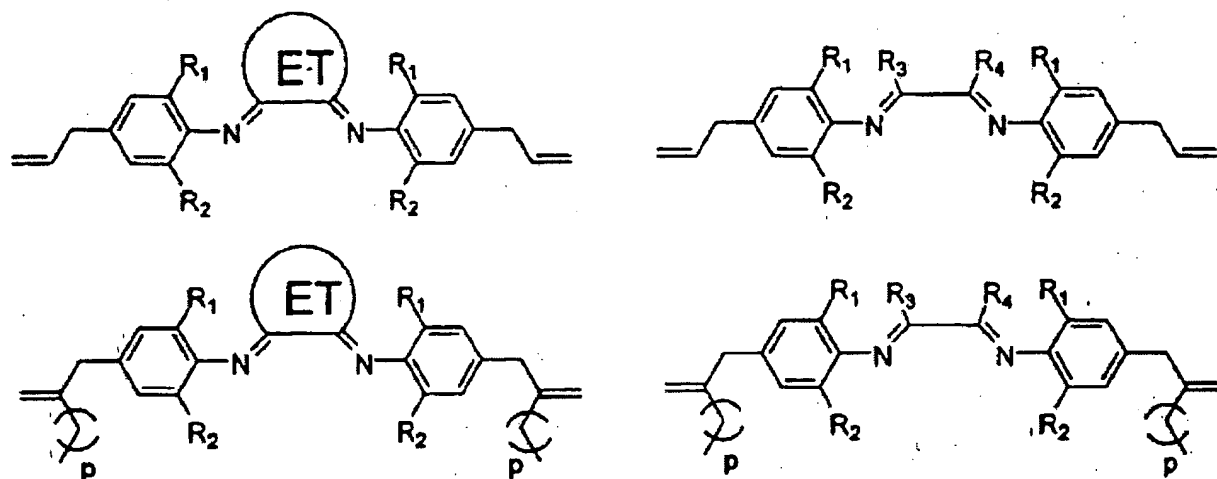
2. A method for preparing component A of the polymerized "post-MAO"  $\alpha$ -diimide nickel catalysts for olefin polymerization according to the description in Claim 1, comprising:  
under the catalytic action of formic acid, acetic acid,  $\text{CF}_3\text{COOH}$  and hydrochloric acid,  
and in a solvent system of acid and alcohol,  $\alpha$ -diketones having the following formulas,



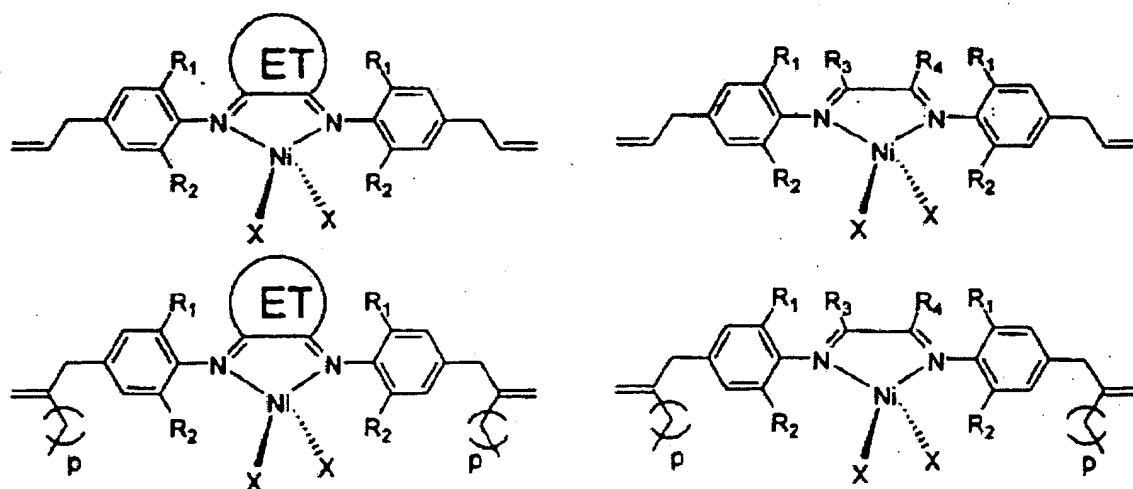
undergo condensation reactions with alkenyl-substituted arylamines represented by the following formulas,



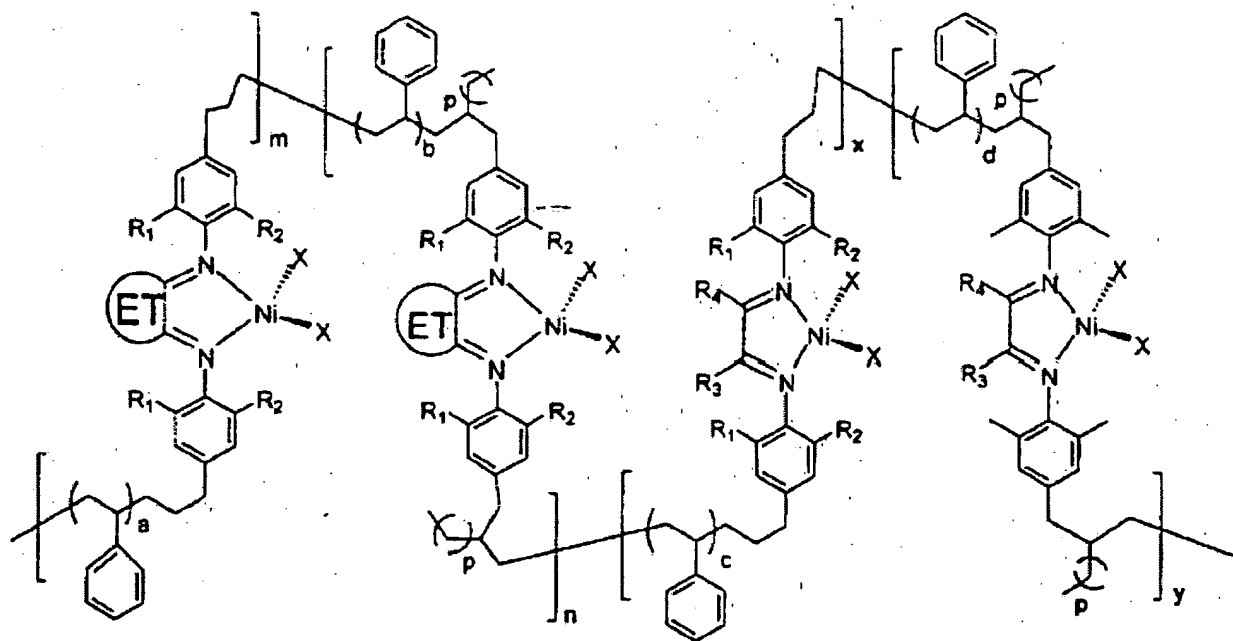
to give  $\alpha$ -diimide ligands having alkenyl groups represented by the following formulas,



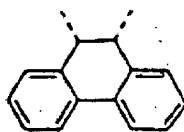
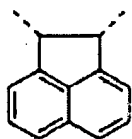
under anhydrous and oxygen-free conditions, a coordination reaction of the aforementioned ligands and  $\text{NiX}_2$ , where  $x$  is Cl or Br, is carried out to give  $\alpha$ -diimide Ni(II) coordination compounds containing alkenyl groups represented by the following formulas,



copolymerization of the  $\alpha$ -diimide Ni(II) coordination compounds containing alkenyl groups and styrene initiated by AIBN is then carried out under anhydrous and oxygen-free conditions, to link the catalysts to the polyethylene [sic; polystyrene] chains through  $\sigma$  bonding, to give the polymerized "post-MAO" catalysts of the following formula for olefin polymerization.



where M represents Ni; x is Cl or Br; p is an integer of 0-4; a, b, c, d, m, n, x and y are integers of 0-150; R<sub>1</sub> and R<sub>2</sub> may be the same or different and represent H, methyl groups, isopropyl groups or tert-butyl groups; R<sub>3</sub> and R<sub>4</sub> may be the same or different and represent methyl groups, ethyl groups, propyl groups or heterocyclic groups, and ET is selected from the following divalent residues of cyclic compounds or mixtures thereof:



SiO<sub>2</sub> represents a silicon dioxide carrier immobilizing polymerized catalyst [P(S-co-Cat)].

Component B is selected from methylaluminoxane and pentafluorobromobenzene [B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>].

3. The method for preparing the polymerized "post-MAO"  $\alpha$ -diimide nickel catalysts for olefin polymerization according to the description of Claims 1 and 2, characterized in that in the process of preparing component A of the SiO<sub>2</sub>-carried polymerized "post-MAO"  $\alpha$ -diimide nickel catalysts for olefin polymerization, SiO<sub>2</sub> carrier, solvent and catalyst are added first, and an initiator is added after the temperature is increased to 70°C, followed by carrying out polymerization for 8 h at a constant 80°C.

4. The method for preparing the polymerized "post-MAO"  $\alpha$ -diimide nickel catalyst for olefin polymerization according to the description of Claim 1, characterized in that the process of producing polyethylene includes a process utilizing said component A of the polymerized "post-MAO"  $\alpha$ -diimide nickel(II) catalysts for olefin polymerization according to description of Claim 1.

5. The method for preparing the polymerized "post-MAO"  $\alpha$ -diimide nickel catalysts for olefin polymerization according to the description of Claim 1, characterized in that the polymerization pressure for producing polyethylene is 1-20 atm.

6. The method for preparing the polymerized "post-MAO"  $\alpha$ -diimide nickel catalysts for olefin polymerization according to the description of Claim 1, characterized in that production of polyethylene is carried out by homogeneous or heterogeneous polymerization.

### Specifications

#### Technical field

This patent pertains to a catalyst for olefin polymerization, particularly a polymerized "post-MAO" transition metal catalyst containing alkenyl groups for olefin polymerization.

The present invention also pertains to a preparation method for the aforementioned catalyst.

The present invention also pertains to the application of the aforementioned catalyst for olefin polymerization, particularly for ethylene polymerization.

#### Prior art

Beginning in the 1990s, the "post-MAO" late-transition metal catalysts have been lauded as the 3<sup>rd</sup> generation of catalysts with a high activity for olefin polymerization after Ziegler-Natta catalysts and metallocene catalysts, and they have become the focal point of world-wide research on new catalysts for olefin polymerization. Different from the traditional Ziegler-Natta catalysts and metallocene catalysts, most late-transition metal catalysts are only suitable for ethylene dimerization or oligomerization due to the  $\beta$ -H eliminating reaction, and high molecular weight polyethylenes cannot be produced by them. Recently, the Brookhart research group supported by Du Pont Company (J. Am. Chem. Soc., 122 6686 (2000), 121 10634 (1999), 120 888 (1998), 118 267 (1996), 117 6414 (1995); Macromolecules, 31, 6705 (1998); US 5,886,223, US 5,891,563) published a series of late-transition metal nickel and palladium  $\alpha$ -diimide compounds, capable of polymerizing ethylene and  $\alpha$ -olefins into high molecular weight polymers having characteristic microstructures. This pioneering development work opened a new area of research on catalysts for olefin polymerization.

These type of Ni(II) and palladium(II) diimide compounds show a higher activity for ethylene polymerization under the action of the auxiliary catalyst MAO, and the activity can reach to the same level as that of metallocene catalysts, with some reaching  $1.1 \times 10^4$  kg PE/(mol  $\cdot$  Ni  $\cdot$  h); also, by using this type of new diimide Ni(II) catalyst, not only can ethylene be polymerized to give high density polyethylene and polyethylene with a medium degree of branching with methyl groups as the main branches, but  $\alpha$ -olefins and cycloolefins can also be



polymerized in equal quantity to give high molecular weight polymers; additionally, palladium diimide compounds achieve true copolymerization of olefins and methyl acrylate for the first time; what should be noted is that, by varying and controlling the pressure, temperature and ligand substituent, polyethylenes ranging from homopolymers having a high degree of branching and high irregularity to those of linear, semicrystalline and high density can be produced. Research on polymerization with this type of catalyst cannot be found in the literature, and research on such polymerizing technique has a certain positive implication for better control of polymerization with this type of catalyst and for increasing the catalytic activity so that polymers with ideal molecular weight and degree of branching can be produced, while having better adaptation to industrial production equipment.

#### Objective of the invention

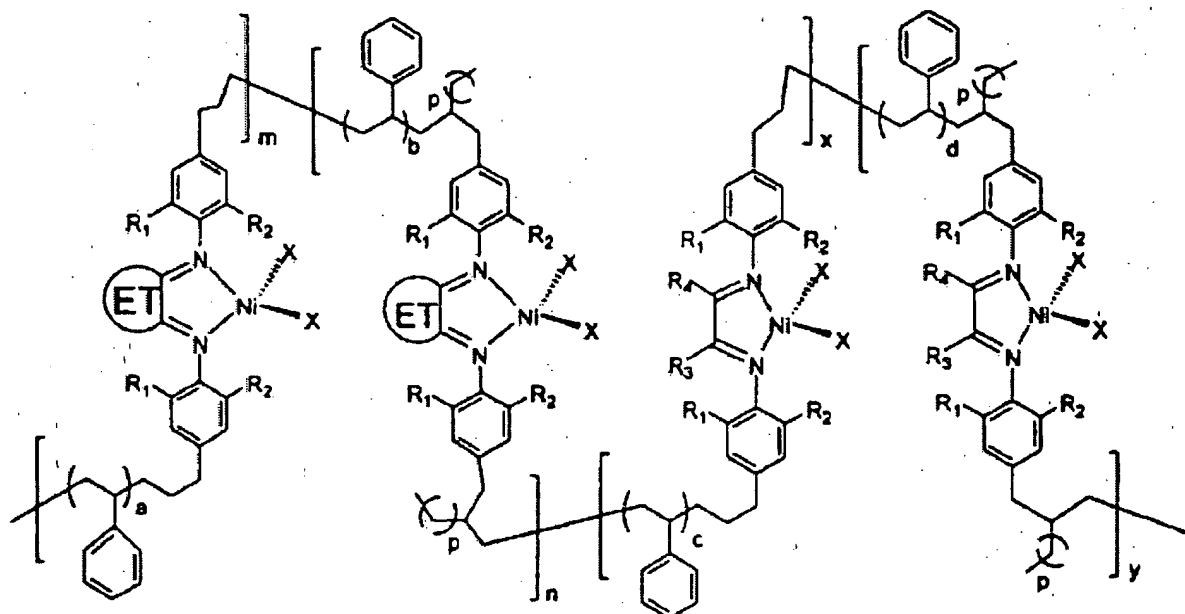
The objective of the present invention lies in providing a polymerized "post-MAO"  $\alpha$ -diimide nickel catalyst for olefin polymerization.

Another objective of the present invention lies in providing a method of preparing a polymerized "post-MAO" catalyst for olefin polymerization; said method utilizes an alkenyl group-substituted  $\alpha$ -diimide nickel compound and styrene to link the "post-MAO" catalyst into polymer chain through  $\sigma$  bonding via the action of an initiator to form said polymerized "post-MAO" catalyst for olefin polymerization.

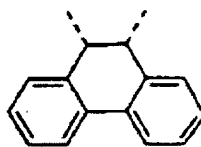
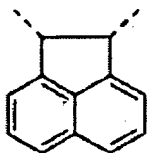
Still another objective of the present invention lies in providing a polymerized "post-MAO"  $\alpha$ -diimide nickel catalyst for application in olefin polymerization, particularly ethylene polymerization.

Polymerized "post-MAO"  $\alpha$ -diimide nickel catalysts also possess a very high activity in olefin polymerization, and polymerizing "post-MAO" catalysts allows easy control of the composition and distribution of catalysts on polymer chains, and the catalytic effect of the active center can be exercised to the fullest by regulating the distribution of catalysts on the polymer chains. Additionally, polymers obtained by olefin polymerization using polymerized "post-MAO"  $\alpha$ -diimide nickel catalysts do not contain inorganic ash.

The catalysts prepared by the present invention comprise components A and B, in that component A is expressed by the formula  $[P(S\text{-}co\text{-}Cat)]$  or  $SiO_2\text{-}P(S\text{-}co\text{-}Cat)$ , where P represents a copolymer, S is polystyrene, co represents copolymerization, Cat represents 1-4 kinds of "post-MAO"  $\alpha$ -diimide nickel catalysts containing alkenyl groups.  $[P(S\text{-}co\text{-}Cat)]$  are copolymers of 1-4 kinds of  $\alpha$ -diimide nickel catalysts and styrene, having the following structure:



Where M represents Ni; x is Cl or Br; p is an integer of 0-4; a, b, c, d, m, n, x and y are integers of 0-150;  $R_1$  and  $R_2$  may be the same or different and represent H, methyl groups, isopropyl groups or tert-butyl groups;  $R_3$  and  $R_4$  may be the same or different and represent methyl groups, ethyl groups, propyl groups or heterocyclic groups, and ET is selected from the following divalent residues of cyclic compounds or mixtures thereof.

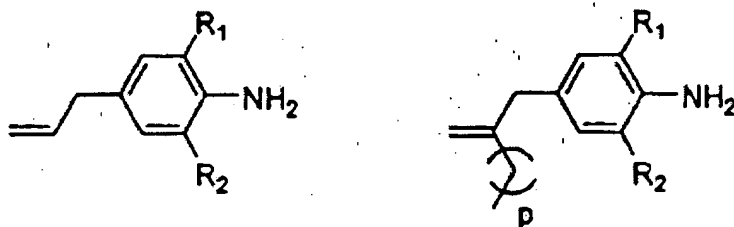


$\text{SiO}_2$  represents a silicon dioxide carrier immobilizing the polymerized catalyst [P(S-co-Cat)]. Component B is selected from methylaluminoxane and boron pentafluorobromobenzene [ $\text{B}(\text{C}_6\text{F}_5)_3$ ].

The catalyst preparation procedure is as follows:

N-alkenylanilines formed from substituted aromatic amines and alkenyl chlorides or alkenyl bromides are rearranged to give 4-alkenylarylamines in the presence of anhydrous zinc chloride, giving yields of 25-71%.

The structures are:

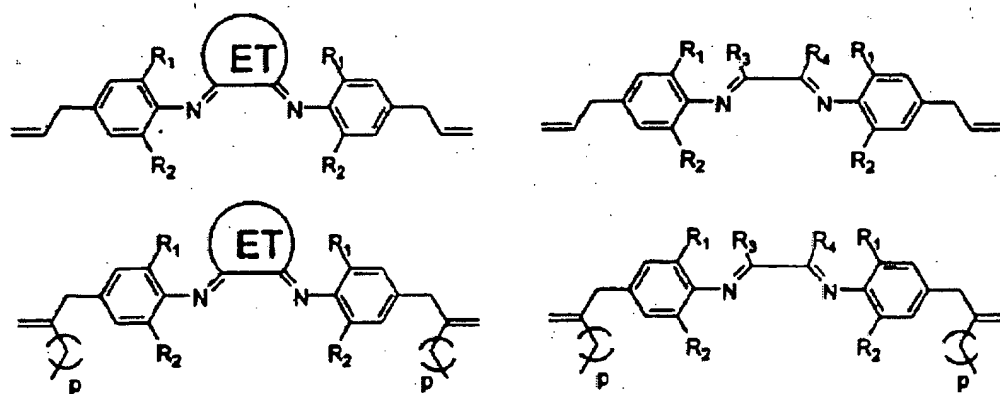


Where  $R_1$  and  $R_2$  may be the same or different and represent H, methyl groups, isopropyl groups, or tert-butyl groups, and  $p$  is an integer of 0-4.

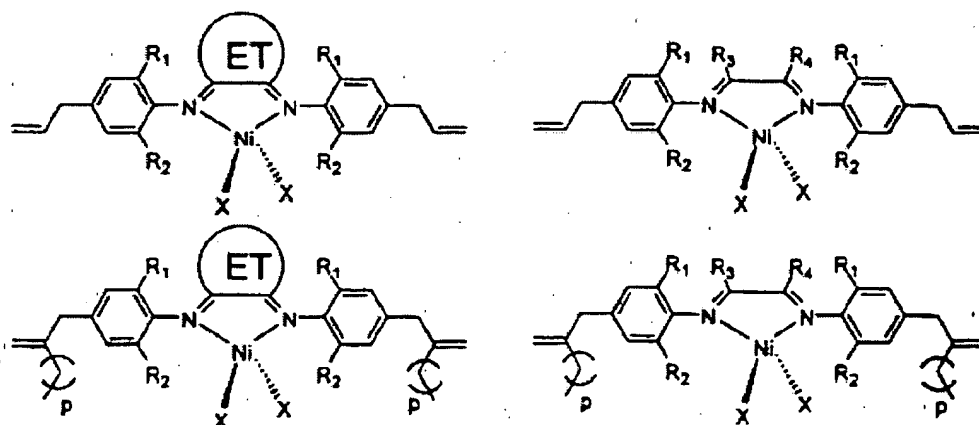
They undergo a condensation reaction with a  $\alpha$ -diketone of the following formulas in a solvent system of acid and alcohol, under the catalytic action of formic acid, acetic acid,  $\text{CF}_3\text{COOH}$  and hydrochloric acid.



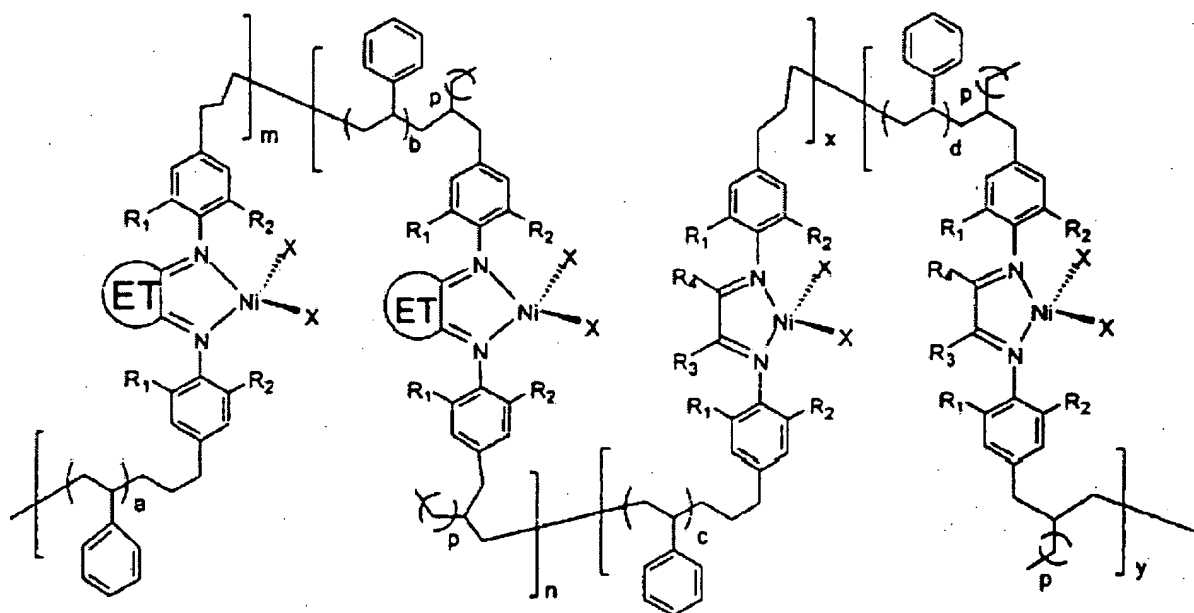
$\alpha$ -diimide ligands having alkenyl groups represented by the following formulas are obtained, yield 72-84%:



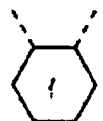
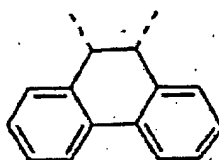
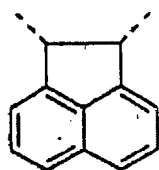
The coordination reaction of the aforementioned ligands and  $\text{NiX}_2$ , where  $x$  is Cl or Br, is carried out under anhydrous and oxygen-free conditions, to give  $\alpha$ -diimide Ni(II) coordination compounds containing alkenyl groups represented by the following formulas, yield 92-98%;



Copolymerization of the  $\alpha$ -diimide Ni(II) coordination compounds containing alkenyl groups and styrene initiated by AIBN is then carried out under anhydrous and oxygen-free conditions, to link the catalysts to the polyethylene [sic; polystyrene] chains through  $\sigma$  bonding, to give the polymerized "post-MAO" catalysts of the following formula for olefin polymerization;



where M represents Ni; x is Cl or Br; p is an integer of 0-4; a, b, c, d, m, n, x and y are integers of 0-150;  $R_1$  and  $R_2$  may be the same or different and represent H, methyl groups, isopropyl groups or tert-butyl groups;  $R_3$  and  $R_4$  may be the same or different and represent methyl groups, ethyl groups, propyl groups or heterocyclic groups, and ET is selected from the following divalent residues of cyclic compounds or mixtures thereof:



$\text{SiO}_2$  represents a silicon dioxide carrier immobilizing the polymerized catalyst  $[\text{P}(\text{S-co-Cat})]$ .

Component A catalyzes polymerization of olefins at 1-20 atm, via the aid of auxiliary catalyst component B, where component B represents methylaluminoxane or boron pentafluorobromobenzene  $[\text{B}(\text{C}_6\text{F}_5)_3]$ , and the numerical activity level is  $10^5$ - $10^7$ /g PE/(mol·Ni·h) [sic; mol Ni·h].

The specific application examples are as follows:

#### Application Example 1: Preparation of allylarylamines

A mixture of 2,6-diisopropylaniline 0.2 mol and allyl chloride 0.1 mol is heated and refluxed for 8 h, followed by cooling and allowing to stand overnight, and is then added to 400 mL water and made alkaline with a sodium hydroxide solution, and the reaction mixture is extracted with diethyl ether. Vacuum distillation to give N-allyl-2,6-diisopropylaniline, 18.33 g, yield 84%. N-allyl-2,6-diisopropylaniline 0.084 mol and anhydrous zinc chloride 0.1 mol are added to 100 mL toluene solvent, which is refluxed for 5 h under an argon atmosphere, and the mixture is made alkaline with aqueous sodium hydroxide solution after cooling. The organic layer is separated and the insoluble material in the lower layer is dissolved in hot concentrated hydrochloric acid, which is decanted into the aforementioned diethyl ether extract solution, followed by drying over anhydrous magnesium sulfate and vacuum distillation to give 4-allyl-2,6-diisopropylaniline, 12.92 g, yield 71%.

#### Application Example 2: Preparation of allylarylamines

A mixture of 2-tert-butylaniline 0.1 mol and 1-bromo-2-butene 0.05 mol is heated and refluxed for 10 h, followed by cooling and allowing to stand overnight, and then added to 200 mL water and made alkaline with a sodium hydroxide solution, and the reaction mixture is extracted with diethyl ether. Vacuum distillation to give, N-(2-methylallyl)-2-tert-butylaniline, 5.35 g, yield 53%. N-(2-methylallyl)-2-tert-butylaniline 0.2 mol and anhydrous zinc chloride 0.2 mol are added to 200 mL toluene solvent, which is refluxed for 8 h under an argon atmosphere, and the mixture is made alkaline with an aqueous sodium hydroxide solution after cooling. The organic layer is separated and the insoluble material in the lower layer is dissolved in hot concentrated hydrochloric acid, which is decanted into the aforementioned diethyl ether

extract solution, followed by drying over anhydrous magnesium sulfate and vacuum distillation to give 4-(2-methylallyl)-2-tert-butaniline, 24.89 g, yield 61%.

#### Application Example 3: Preparation of allylarylamines

A mixture of 2,6-dimethylaniline 0.12 mol and 1-bromo-2-pentene 0.06 mol is heated and refluxed for 9 h, followed by cooling and allowing to stand overnight, and is then added to 300 mL water and made alkaline with a sodium hydroxide solution, and the reaction mixture is extracted with diethyl ether. Vacuum distillation to give N-(2-ethylallyl)-2,6-dimethylaniline, 3.72 g, yield 33%. N-(2-ethylallyl)-2,6-dimethylaniline 0.05 mol and anhydrous zinc chloride 0.05 mol are added to 80 mL toluene solvent, which is refluxed for 7 h under an argon atmosphere, and the mixture is made alkaline with aqueous sodium hydroxide solution after cooling. The organic layer is separated and the insoluble material in the lower layer is dissolved in hot concentrated hydrochloric acid, which is decanted into the aforementioned diethyl ether extract solution, followed by drying over anhydrous magnesium sulfate and vacuum distillation to give 4-allyl-2,6-dimethylaniline [sic; 4-(2-ethylallyl)-2,6-dimethylaniline], 2.77 g, yield 29%.

#### Application Example 4: Preparation of allylarylamines

A mixture of 2,6-diisopropylaniline 0.1 mol and 1-bromo-2-heptene 0.05 mol is heated and refluxed for 10 h, followed by cooling and allowing to stand overnight, and then added to 300 mL water and made alkaline with a sodium hydroxide solution, and the reaction mixture is extracted with diethyl ether. Vacuum distillation to give N-(2-butylallyl)-2,6-diisopropylaniline, 4.09 g, yield 30%. N-(2-butylallyl)-2,6-diisopropylaniline 0.05 mol and anhydrous zinc chloride 0.05 mol are added to 50 mL toluene solvent, which is refluxed for 8 h under an argon atmosphere, and the mixture is made alkaline with a aqueous sodium hydroxide solution after cooling. The organic layer is separated and the insoluble material in the lower layer is dissolved in hot concentrated hydrochloric acid, which is decanted into the aforementioned diethyl ether extract solution, followed by drying over anhydrous magnesium sulfate and vacuum distillation to give 4-(2-butylallyl)-2,6-diisopropylaniline, 3.44 g, yield 25%.

#### Application Example 5: Preparation of diimide bidentate ligands containing two alkenyl groups

2 mmol  $\alpha$ -Acenaphthenone and 4 mmol 4-allyl-2,6-diisopropylaniline are dissolved in 20 mL acetic acid, which is heated and refluxed for 1 h, followed by cooling to room temperature to give a solid precipitate, which is filtered and washed in sequence with acetic acid (3 x 20 mL) and n-hexane (3 x 20 mL), and vacuum dried to give  $\alpha$ -diimide ligand compound  $C_{42}H_{48}N_2$ , 1.0 g, yield 84%.

Application Example 6: Preparation of diimide bidentate ligands containing two alkenyl groups

$\alpha$ -Butadione 3 mmol and 4-(2-methylallyl)-2-tert-butyraniline 6 mmol are dissolved in 30 mL methanol, which is heated and refluxed for 1 h after adding 3-5 drops of formic acid as the catalyst, followed by cooling to room temperature to give a solid precipitate, which is filtered and washed in sequence with methanol (3 x 20 mL) and n-hexane (3 x 20 mL) and vacuum dried to give  $\alpha$ -diimide ligand compound  $C_{36}H_{52}N_2$ , 1.2 g, yield 80%.

Application Example 7: Preparation of diimide bidentate ligands containing two alkenyl groups

$\alpha$ -Cyclohexadione 2.5 mmol and 4-allyl-2,6-dimethylaniline 5 mmol are dissolved in 25 mL ethanol, which is heated and refluxed for 1 h after adding 3-5 drops of hydrochloric acid as the catalyst, followed by cooling to room temperature to give a solid precipitate, which is filtered and washed in sequence with ethanol (3 x 20 mL) and n-hexane (3 x 20 mL) and vacuum dried to give  $\alpha$ -diimide ligand compound  $C_{28}H_{34}N_2$ , 1.0 g, yield 72%.

Application Example 8: Preparation of diimide bidentate ligands containing two alkenyl groups

$\alpha$ -Phenanthradione 2.5 mmol and 4-(2-butylallyl)-2,6-diisopropylaniline 5 mmol are dissolved in 30 mL methanol, which is heated and refluxed for 1 h, followed by cooling to room temperature to give a solid precipitate, which is filtered and washed in sequence with methanol (3 x 20 mL) and n-hexane (3 x 20 mL) and vacuum dried to give  $\alpha$ -diimide ligand compound  $C_{52}H_{66}N_2$ , 1.5 g, yield 82%.

Application Example 9: Preparation of  $\alpha$ -diimide nickel catalysts containing two alkenyl groups

Preparation of the catalyst is carried out under the protective conditions of oxygen-free, moisture-free and high purity argon. The diimide ligand obtained in Application Example 5 (1 mmol) and 1 mmol  $[Ni(DME)Br_2]$  (DME: dimethyl diethylether) are agitated in 30 mL dichloromethane solvent for 12 h at room temperature, followed by vacuum distillation to remove the solvent, and the precipitate is washed 3-5 times with 50 mL ether and vacuum dried to give  $\alpha$ -diimide nickel catalyst  $C_{42}H_{48}N_2NiBr_2$ , 0.8 g, yield 98%.

Application Example 10: Preparation of  $\alpha$ -diimide nickel catalysts containing two alkenyl groups

Preparation of the catalyst is carried out under the protective conditions of oxygen-free, moisture-free and high purity argon. The diimide ligand obtained in Application Example 6 (1 mmol) and 1 mmol  $[Ni(DME)Cl_2]$  (DME: dimethyl diethyl ether) are agitated in 40 mL dichloromethane solvent for 48 h at room temperature, followed by vacuum distillation to remove the solvent, and the precipitate is washed 3-5 times with 50 mL ether and vacuum dried to give  $\alpha$ -diimide nickel catalyst  $C_{36}H_{52}N_2NiCl_2$ , 0.6 g, yield 98%.

Application Example 11: Preparation of  $\alpha$ -diimide nickel catalysts containing two alkenyl groups

Preparation of the catalyst is carried out under the protective conditions of oxygen-free, moisture-free and high purity argon. The diimide ligand obtained in Application Example 7 0.05 mmol and 0.05 mmol  $[\text{Ni}(\text{DME})\text{Br}_2]$  (DME: dimethyl diethyl ether) are agitated in 30 mL dichloromethane solvent for 24 h at room temperature, followed by vacuum distillation to remove the solvent, and the precipitate is washed 3-5 times with 50 mL ether and vacuum dried to give  $\alpha$ -diimide nickel catalyst  $\text{C}_{28}\text{H}_{34}\text{N}_2\text{NiCl}_2$ , 0.3 g, yield 96%.

Application Example 12: Preparation of  $\alpha$ -diimide nickel catalysts containing two alkenyl groups

Preparation of the catalyst is carried out under the protective conditions of oxygen-free, moisture-free and high purity argon. The diimide ligand obtained in Application Example 8 1 mmol and 1 mmol  $[\text{Ni}(\text{DME})\text{Cl}_2]$  (DME: dimethyl diethyl ether) are agitated in 30 mL dichloromethane solvent for 72 h at room temperature, followed by vacuum distillation to remove the solvent, and the precipitate is washed 3-5 times with 50 mL ether and vacuum dried to give  $\alpha$ -diimide nickel catalyst  $\text{C}_{42}\text{H}_{64}\text{N}_2\text{NiCl}_2$ , 0.7 g, yield 92%.

Application Example 13: Preparation of component A of polymerized "post-MAO"  $\alpha$ -diimide nickel catalysts

Under oxygen-free and anhydrous conditions, "post-MAO"  $\alpha$ -diimide nickel catalyst  $\text{C}_{42}\text{H}_{48}\text{N}_2\text{NiBr}_2$  containing alkenyl groups (2 mmol) obtained in Application Example 9, styrene 5 mL and azobisisobutyronitrile 0.05 g are added in sequence to predistilled toluene and mixed until homogeneous, which is then polymerized for 12 h on an 80°C water bath. The mixture is concentrated by heating and the precipitates are washed 3-5 times with n-hexane and vacuum dried to give catalyst component A  $\text{P}[\text{S-co-(C}_{42}\text{H}_{48}\text{N}_2\text{NiBr}_2)]$ , for which the nickel content is found to be 0.284 wt%.

Application Example 14: Preparation of component A of polymerized "post-MAO"  $\alpha$ -diimide nickel catalysts

Under oxygen-free and anhydrous conditions, "post-MAO"  $\alpha$ -diimide nickel catalyst  $\text{C}_{36}\text{H}_{52}\text{N}_2\text{NiCl}_2$  containing alkenyl groups (10 mmol) obtained in Application Example 10, styrene 10 mL and azobisisobutyronitrile 0.14 g are added in sequence to predistilled toluene and mixed until homogeneous, then polymerized for 15 h on an 80°C water bath. The mixture is concentrated by heating and the precipitates are washed 3-5 times with n-hexane and vacuum dried to give catalyst component A  $\text{P}[\text{S-co-(C}_{36}\text{H}_{52}\text{N}_2\text{NiCl}_2)]$ , for which the nickel content is found to be 0.258 wt%.



Application Example 15: Preparation of component A of polymerized "post-MAO"  $\alpha$ -diimide nickel catalyst

Under oxygen-free and anhydrous conditions, "post-MAO"  $\alpha$ -diimide nickel catalysts obtained in Application Examples 9 and 10,  $C_{42}H_{48}N_2NiBr_2$  and  $C_{36}H_{52}N_2NiCl_2$  containing alkenyl groups (5 mmol each), styrene 10 mL and azobisisobutyronitrile 0.14 g are added in sequence to predistilled toluene and mixed until homogeneous, then polymerized for 15 h on an 80°C water bath. The mixture is concentrated by heating and the precipitates are washed 3-5 times with n-hexane, and vacuum dried to give catalyst component A  $P[S-co-(C_{42}H_{48}N_2NiBr_2)-co-(C_{36}H_{52}N_2NiCl_2)]$ , for which the nickel content is found to be 0.228 wt%.

Application Example 16: Preparation of component A of polymerized "post-MAO"  $\alpha$ -diimide nickel catalyst with silicon dioxide carrier

Under oxygen-free and anhydrous conditions, 5 g silicon dioxide carrier are weighed and dried under vacuum for 12 h, which together with "post-MAO"  $\alpha$ -diimide nickel catalyst  $C_{42}H_{48}N_2NiBr_2$  containing alkenyl groups (2 mmol) obtained in Application Example 9, styrene 5 mL and azobisisobutyronitrile 0.05 g are added in sequence to predistilled toluene and mixed until homogeneous, then polymerized for 12 h on a 80°C water bath. The mixture is concentrated by heating and the precipitates are washed 3-5 times with n-hexane and vacuum dried to give catalyst component A  $SiO_2-P[S-co-(C_{42}H_{48}N_2NiBr_2)]$ , for the nickel content is found to be 0.158 wt%.

Application Example 17: Preparation of polymerized "post-MAO"  $\alpha$ -diimide nickel catalyst with silicon dioxide carrier

Under oxygen-free and anhydrous conditions, 10 g silicon dioxide carrier are weighed and vacuum dried for 12 h, which together with "post-MAO"  $\alpha$ -diimide nickel catalyst  $C_{36}H_{52}N_2NiCl_2$  containing alkenyl groups (10 mmol) obtained in Application Example 9 [sic] and 10, styrene 10 mL and azobisisobutyronitrile 0.14g are added in sequence to predistilled toluene and mixed until homogeneous, then polymerized for 12 h on an 80°C water bath. The mixture is concentrated by heating and the precipitates are washed 3-5 times with n-hexane and vacuum dried to give catalyst component A  $SiO_2-P[S-co-(C_{36}H_{52}N_2NiCl_2)]$ , for which the nickel content is found to be 0.147 wt%.

Application Example 18: Preparation of polymerized "post-MAO"  $\alpha$ -diimide nickel catalyst with silicon dioxide carrier

Under oxygen-free and moisture-free conditions, 10 g silicon dioxide carrier are weighed and vacuum dried for 12 h, which together with "post-MAO"  $\alpha$ -diimide nickel catalysts obtained in Application Examples [9 and] 10,  $C_{42}H_{48}N_2NiBr_2$  and  $C_{36}H_{52}N_2NiCl_2$  containing alkenyl groups (5 mmol each), styrene 10 mL and azobisisobutyronitrile 0.14 g are added in sequence to predistilled toluene and mixed until homogeneous, then polymerized for 12 h on a 80°C water bath. The mixture is concentrated by heating and the precipitates are washed 3-5 times with n-hexane and vacuum dried to give catalyst component A  $SiO_2$ -P[S-co- $(C_{42}H_{48}N_2NiBr_2)$ -co- $(C_{36}H_{52}N_2NiCl_2)$ ], for which the nickel content is found to be 0.153 wt%.

Application Example 19: Homogeneous and heterogeneous polymerizations of ethylene

Polymerization of ethylene is carried out under oxygen-free and anhydrous conditions. The reaction system comprises toluene 50 mL, to which methylaluminoxane 0.45 mL, polymerized catalyst P[S-co- $(C_{42}H_{48}N_2NiBr_2)$ ] obtained in Application Example 13 (1 mmol) (based on Al/Ni = 1000) and ethylene are added in sequence and reaction is carried out for 0.5 h at 20°C. The reaction is quenched using an ethanol solution containing 1% hydrochloric acid, and the obtained product is filtered, washed 3 times with ethanol, followed by vacuum drying for 24 h at 40°C, to give 0.56 g polyethylene, activity  $1.12 \times 10^6$  g PE/(mol Ni · h).

Application Example 20: Homogeneous and heterogeneous polymerizations of ethylene

The same operation as in Application Example 19 is carried out with methylaluminoxane 1.8 mL (based on Al/Ni = 4000), to give 0.78 g polyethylene, activity  $1.56 \times 10^6$  g PE/(mol Ni · h).

Application Example 21: Homogeneous and heterogeneous polymerizations of ethylene

The same operation as in Application Example 19 is carried out with methylaluminoxane 1.48 mL (based on Al/Ni = 1000), to give 0.87 g polyethylene, activity  $1.74 \times 10^6$  g PE/(mol Ni · h).

Application Example 22: Homogeneous and heterogeneous polymerizations of ethylene

Polymerization of ethylene is carried out under oxygen-free and anhydrous conditions. The reaction system comprises toluene 50 mL, to which methylaluminoxane 0.45 mL, polymerized catalyst P[S-co- $(C_{42}H_{48}N_2NiBr_2)$ -co- $(C_{36}H_{52}N_2NiCl_2)$ ] obtained in Application Example 15 (1  $\mu$ mol) (based on Al/Ni = 1000) and ethylene are added in sequence and reaction is carried out for 0.5 h at 20°C. The reaction is quenched using an ethanol solution containing

1% hydrochloric acid, and the obtained product is filtered, washed 3 times with ethanol, followed by vacuum drying for 24 h at 40°C, to give 0.51 g polyethylene, activity  $1.1 \times 10^6$  g PE/(mol Ni · h).

Application Example 23: Homogeneous and heterogeneous polymerizations of ethylene

Polymerization of ethylene is carried out under oxygen-free and anhydrous conditions. The reaction system comprises toluene 50 mL, to which methylaluminoxane 1.6 mL, polymerized catalyst P[S-co-(C<sub>42</sub>H<sub>48</sub>N<sub>2</sub>NiBr<sub>2</sub>)-co-(C<sub>36</sub>H<sub>52</sub>N<sub>2</sub>NiCl<sub>2</sub>)] obtained in Application Example 15 (1 μmol) (based on Al/Ni = 3500) and ethylene are added in sequence and reaction is carried out for 0.5 h at 0°C. The reaction is quenched using an ethanol solution containing 1% hydrochloric acid, and the obtained product is filtered, washed 3 times with ethanol, followed by vacuum drying for 24 h at 40°C, to give 1.31 g polyethylene, activity  $2.62 \times 10^6$  g PE/(mol Ni · h).

Application Example 24: Homogeneous and heterogeneous polymerizations of ethylene

The same operation as in Application Example 23 is carried out at 60°C, to give 0.31 g polyethylene, activity  $0.62 \times 10^6$  g PE/(mol Ni · h).

Application Example 25: Homogeneous and heterogeneous polymerizations of ethylene

Polymerization of ethylene is carried out under oxygen-free and anhydrous conditions. The reaction system comprises toluene 50 mL, to which methylaluminoxane 1.77 mL, polymerized catalyst SiO<sub>2</sub>-P[S-co-(C<sub>42</sub>H<sub>48</sub>N<sub>2</sub>NiBr<sub>2</sub>)] obtained in Application Example 16 (1.3 μmol) (based on Al/Ni = 3000) and ethylene are added in sequence and reaction is carried out for 0.5 h at 20°C. The reaction is quenched using an ethanol solution containing 1% hydrochloric acid, and the obtained product is filtered, washed 3 times with ethanol, followed by vacuum drying for 24 h at 40°C, to give 0.61 g polyethylene, activity  $0.91 \times 10^6$  g PE/(mol Ni · h).

Application Example 26: Homogeneous and heterogeneous polymerizations of ethylene

The same operation as in Application Example 25 is carried out at an ethylene pressure of 20 atm and 12°C to give 7.31 g polyethylene, activity  $1.11 \times 10^7$  g PE/(mol Ni · h).

Application Example 27: Homogeneous and heterogeneous polymerizations of ethylene

The same operation as in Application Example 25 is carried out with methylaluminoxane 2.43 mL (based on Al/Ni = 4000) to give 0.37 g polyethylene, activity  $0.55 \times 10^6$  g PE/(mol Ni · h).

Application Example 28: Homogeneous and heterogeneous polymerizations of ethylene

The same operation as in Application Example 25 is carried out with methylaluminoxane 1.46 mL (based on Al/Ni = 2500) at an ethylene pressure of 10 atm to give 5.5 g polyethylene, activity  $8.2 \times 10^6$  g PE/(mol Ni · h).

Application Example 29: Homogeneous and heterogeneous polymerizations of ethylene

Polymerization of ethylene is carried out under oxygen-free and anhydrous conditions. The reaction system comprises toluene 50 mL, to which methylaluminoxane 1.77 mL, polymerized catalyst  $\text{SiO}_2\text{-P}[\text{S-co-(C}_{42}\text{H}_{48}\text{N}_2\text{NiBr}_2\text{)-co-(C}_{36}\text{H}_{52}\text{N}_2\text{NiCl}_2\text{)}]$  obtained in Application Example 18 ( $1.3 \mu\text{mol}$ ) (based on Al/Ni = 3500) and ethylene are added in sequence and reaction is carried out for 0.5 h at 20°C. The reaction is quenched using an ethanol solution containing 1% hydrochloric acid, and the obtained product is filtered, washed 3 times with ethanol, followed by vacuum drying for 24 h at 40°C, to give 0.40 g polyethylene, activity  $0.60 \times 10^6$  g PE/(mol Ni · h).

Application Example 30: Homogeneous and heterogeneous polymerizations of ethylene

The same operation as in Application Example 29 is carried out at 12°C to give 0.70 g polyethylene, activity  $1.03 \times 10^6$  g PE/(mol Ni · h).

[19]中华人民共和国国家知识产权局

[51]Int. Cl<sup>7</sup>

C08F 10/00

C08F 4/42

## [12] 发明专利申请公开说明书

[21] 申请号 01140470.1

[43]公开日 2002年6月5日

[11]公开号 CN 1352203A

[22]申请日 2001.12.10 [21]申请号 01140470.1

[71]申请人 中国科学院长春应用化学研究所

地址 130022 吉林省长春市人民大街159号曹桂珍

[72]发明人 金国新 张道

权利要求书4页 说明书14页 附图页数0页

[54]发明名称 高分子化的“茂后” $\alpha$ -双亚胺镍基烯烃聚合催化剂

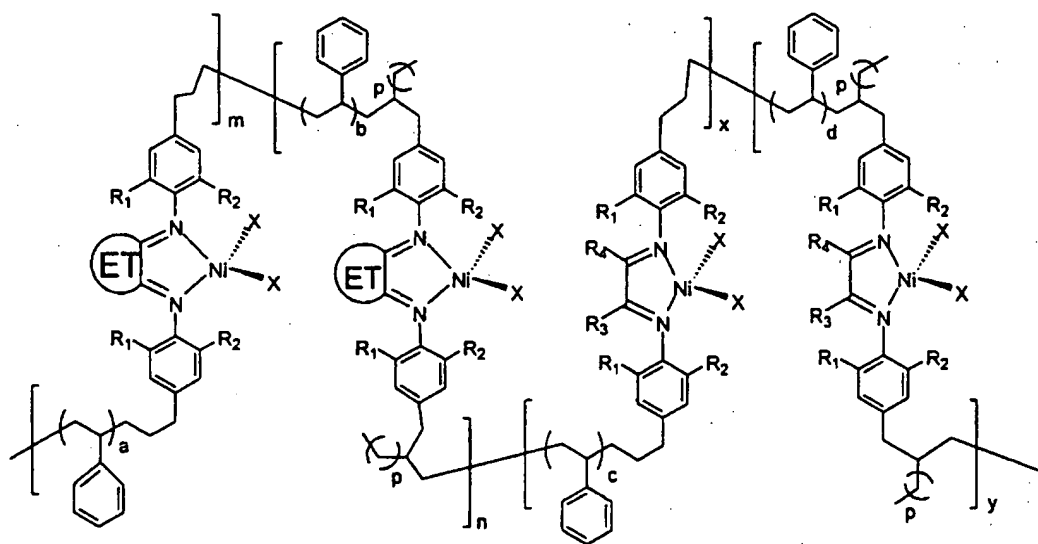
[57]摘要

本发明属于高分子化“茂后” $\alpha$ -双亚胺镍基烯烃聚合催化剂的制备和催化烯烃聚合。催化剂由A和B两组分组成,A组分表达式为 $[P(S-co-Cat)]$ 或 $[SiO_2-P(S-co-Cat)]$ ,P表示共聚物,S为聚苯乙烯,co表示共聚,Cat表示1-4种“茂后” $\alpha$ -双亚胺镍基催化剂,P $(S-co-Cat)$ 是由1-4种 $\alpha$ -双亚胺中性配体与金属Ni所形成的配位化合物,其中胺的对位上含有烯烃基团与苯乙烯共聚得到高分子化“茂后”烯烃聚合催化。SiO<sub>2</sub>表示高分子化 $\alpha$ -双亚胺镍基催化剂 $[P(S-co-Cat)]$ 的二氧化硅载体固载化。B组份为甲基铝氧烷或五氟苯硼 $[B(C_6F_5)_3]$ 其中任意一种。这类催化剂催化乙烯聚合具有较高的活性,适合气相和淤浆聚合工艺,聚合物不含无机灰分。

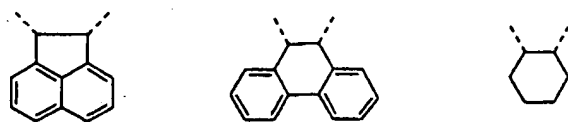
ISSN 1008-4274

## 权 利 要 求 书

1. 一种高分子化的“茂后” $\alpha$ -双亚胺镍基烯烃聚合催化剂，由 A 和 B 两组分组成，其特征在于 A 组分表达式为  $[P(S-co-Cat)]$  或  $[SiO_2-P(S-co-Cat)]$ ，P 表示共聚物，S 为聚苯乙烯，co 表示共聚，Cat 表示 1-4 种含有烯烃基团的“茂后”催化剂， $[P(S-co-Cat)]$  是 1-4 种  $\alpha$ -双亚胺镍基催化剂与苯乙烯的共聚物，它具有如下结构：



其中 M 表示 Ni；X 为 Cl 或 Br；p 为 0-4 的整数；a、b、c、d、m、n、x 和 y 分别为 0-150 的整数；R<sub>1</sub> 与 R<sub>2</sub> 可以相同或不同，分别为 H、甲基、异丙基或叔丁基；R<sub>3</sub> 与 R<sub>4</sub> 可以相同或不同，分别为甲基、乙基、丙基或杂环，ET 是选自下述环状化合物的二价残基或其混合物：

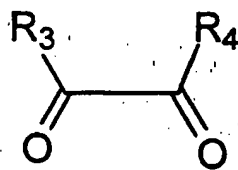
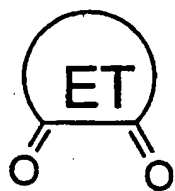


SiO<sub>2</sub> 表示二氧化硅载体将高分子化催化剂  $[P(S-co-Cat)]$  固载化；B

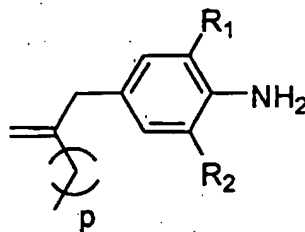
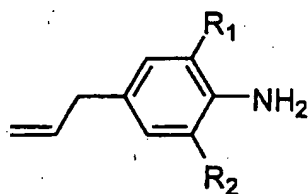
组份为甲基铝氧烷或五氟苯硼[ $B(C_6F_5)_3$ ]其中任意一种。

2. 一种制备权利要求 1 所述的高分子化的“茂后” $\alpha$ -双亚胺镍基烯烃聚合催化剂 A 组分的方法，包括：

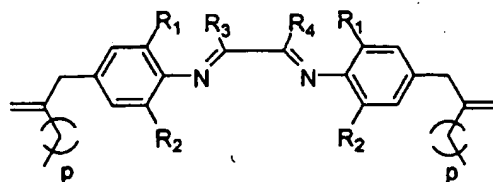
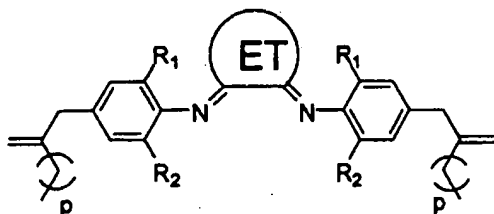
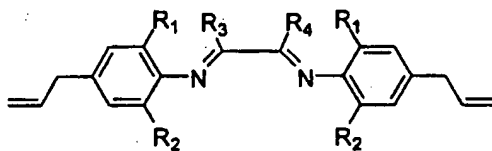
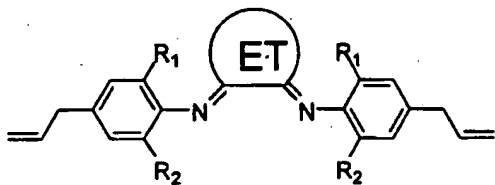
在甲酸、乙酸、 $CF_3COOH$  和盐酸的催化下，在酸和醇溶剂体系中进行下式所述的 $\alpha$ -二酮



与下式所示的烯烃基取代芳胺的缩合反应，

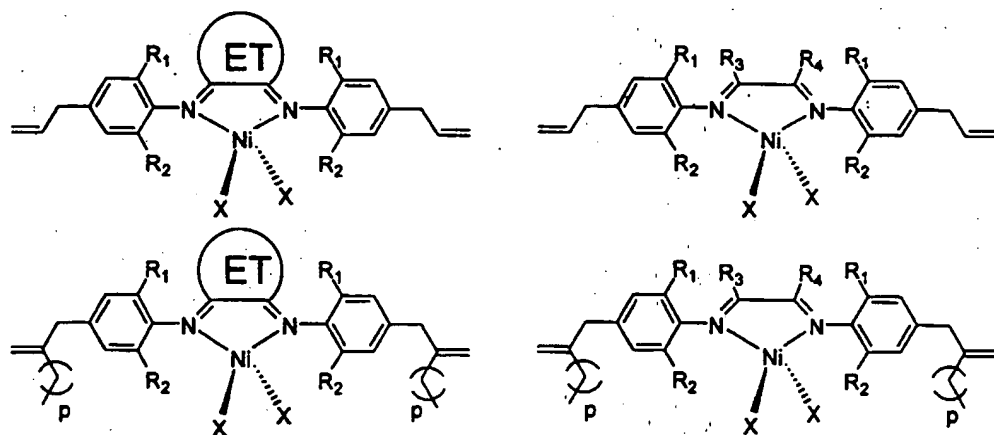


得到下式所示的含有烯烃基团的 $\alpha$ -双亚胺配体：

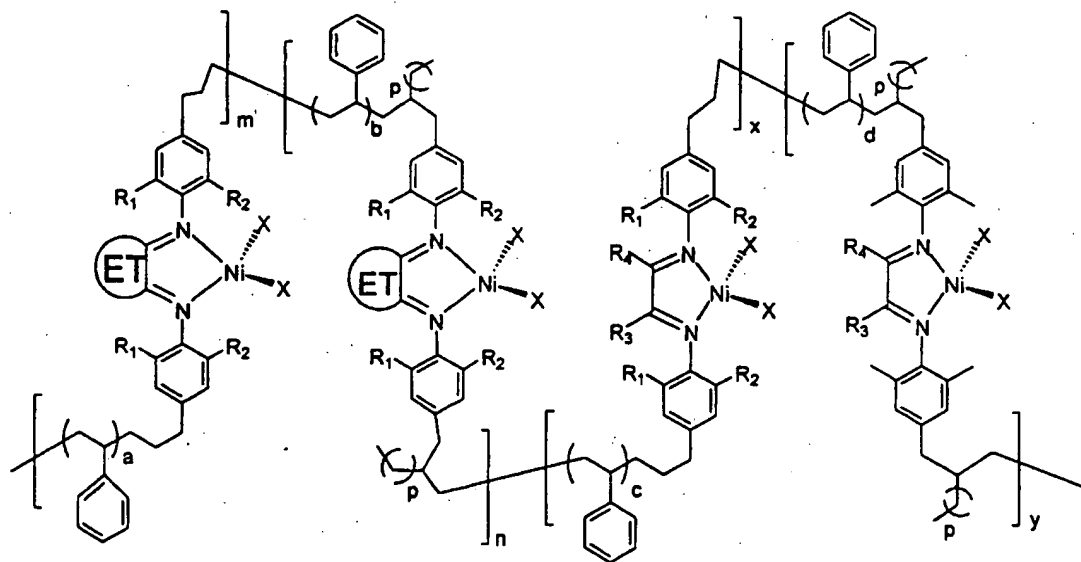


在无水无氧条件下，进行上述配体与  $NiX_2$ ，其中 X 为 Cl 或 Br，的

配位反应，得到下式含有烯烃基团的 $\alpha$ -双亚胺 Ni (II) 配合物，

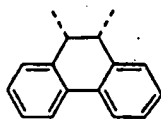
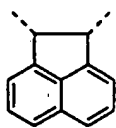


在无水无氧条件下，将含有烯烃基团的 $\alpha$ -双亚胺 Ni (II) 配合物在 AIBN 引发下与苯乙烯共聚，使得催化剂通过  $\sigma$  键与聚乙烯链连结，得到如下式的高分子化“茂后”烯烃聚合催化剂：



其中 M 表示 Ni；X 为 Cl 或 Br；p 为 0-4 的整数；a、b、c、d、m、n、x 和 y 分别为 0-150 的整数； $R_1$  与  $R_2$  可以相同或不同，分别为 H、甲基、异丙基或叔丁基； $R_3$  与  $R_4$  可以相同或不同，分别为甲基、乙基、丙基或杂环，ET 是选自下述环状化合物的二价残基或其混合物：





$\text{SiO}_2$  表示二氧化硅载体将高分子化催化剂  $[\text{P}(\text{S-co-Cat})]$  固载化；B 组份为甲基铝氧烷或五氟苯硼  $[\text{B}(\text{C}_6\text{F}_5)_3]$  其中任意一种。

3. 如权利要求 1、2 所述的高分子化的“茂后” $\alpha$ -双亚胺镍基烯烃聚合催化剂的制备方法，其特征在于二氧化硅负载的高分子化  $\alpha$ -双亚胺镍基催化剂 A 组分的制备过程中，先加入二氧化硅载体、溶剂和催化剂，待温度升至  $70^\circ\text{C}$  后加入引发剂，于  $80^\circ\text{C}$  保温聚合 8 小时。

4. 如权利要求 1 所述的高分子化的“茂后” $\alpha$ -双亚胺镍基烯烃聚合催化剂的制备方法，其特征在于生产聚乙烯过程中，包括使用权利要求 1 所示的高分子化的“茂后” $\alpha$ -双亚胺  $\text{Ni}(\text{II})$  烯烃聚合催化剂 A 组分的步骤。

5. 如权利要求 1 所述的高分子化的“茂后” $\alpha$ -双亚胺镍基烯烃聚合催化剂的制备方法，其特征在于生产聚乙烯的聚合压力为 1-20 atm。

6. 如权利要求 1 所述的高分子化的“茂后” $\alpha$ -双亚胺镍基烯烃聚合催化剂的制备方法，其特征在于生产聚乙烯采用均相聚合和非均相聚合。

高分子化的“茂后” $\alpha$ -双亚胺镍基烯烃聚合催化剂

技术领域：本发明涉及一种烯烃聚合催化剂，具体的涉及一种含有烯根基团的高分子化“茂后”后过渡金属烯烃聚合催化剂；

本发明还涉及一种上述催化剂的制备方法；

本发明还涉及上述催化剂在烯烃聚合中，尤其是在乙烯聚合中的应用。

背景技术：起始于上个世纪末的“茂后”后过渡金属催化剂被誉为继 Ziegler-Natta 催化剂和茂金属催化剂之后的第三代高活性烯烃聚合催化剂，现已成为世界范围内新型烯烃聚合催化剂的研究热点。和传统 Ziegler/Natta 催化剂、茂金属催化剂等不同，由于  $\beta$ -H 的消除反应，大多数后过渡金属催化剂只适合烯烃二聚或齐聚，得不到高分子量的烯烃聚合物。前不久，Du Pont 公司支持的 Brookhart 研究小组 (*J. Am. Chem. Soc.* 122 6686(2000), 121 10634 (1999), 120 888 (1998), 118 267(1996), 117 6414 (1995); *Macromolecules* 31 6705(1998); US 5,886,223, US 5,891,563) 相继报道了一系列后过渡金属镍、钯 $\alpha$ -双亚胺化合物，它们能够将乙烯和 $\alpha$ -烯烃聚合成具有独特微观结构的高分子量聚合物。这一开创性的工作为烯烃聚合催化剂的研究开辟了一个新的领域。

这类 Ni(II)、钯(II)双亚胺类化合物在助催化剂 MAO 的作用下催化乙烯聚合的活性较高，与茂金属催化剂相当，有的可达  $1.1 \times 10^4 \text{ kgPE}/(\text{mol} \cdot \text{Ni} \cdot \text{h})$ ；同时，利用这一类双亚胺 Ni(II)新型

催化剂不仅可以聚合乙烯，得到从高密度聚乙烯到以甲基为主的中等支化度的聚乙烯，还可以使 $\alpha$ -烯烃和环烯烃均聚成高分子量的聚合物；另外，钨的双亚胺化合物首次实现了烯烃与丙烯酸甲酯的真正共聚；值得注意的是，通过改变压力、温度和配体取代基就能可控获得从高度支链化完全无规的乙烯均聚物到线性的、半结晶的高密度乙烯聚合物。这类催化剂的高分子化工作至今未见报道，为了实现这类催化剂的可控聚合，提高催化活性，得到理想分子量和支化度的聚合物，适应工业化生产装置，高分子化的工作有一定的意义。

发明内容：本发明的目的是提供一种高分子化的“茂后” $\alpha$ -双亚胺镍基烯烃聚合催化剂。

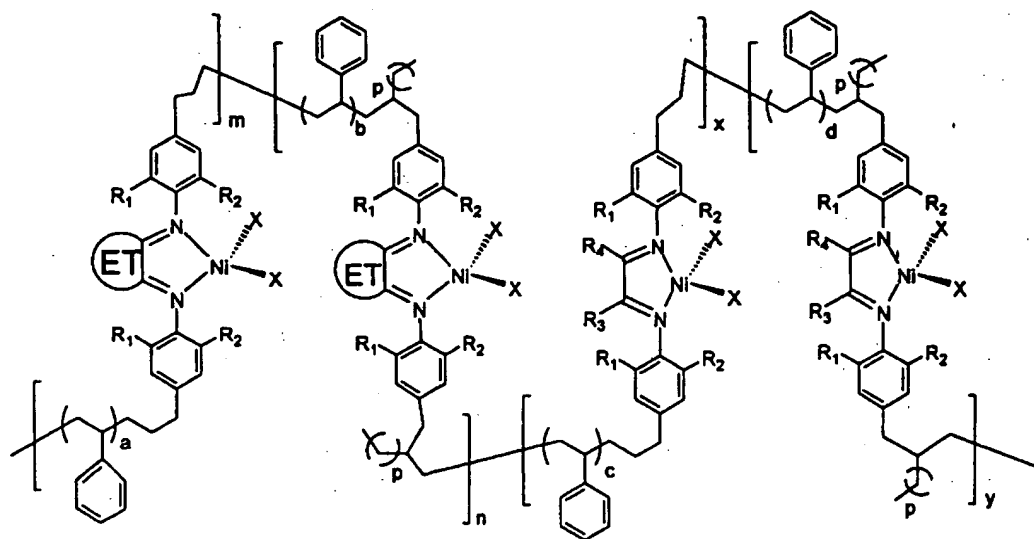
本发明的又一目的是提供一种高分子化的“茂后”烯烃聚合催化剂的制备方法，该方法采用含烯烃取代基团的 $\alpha$ -双亚胺化合物镍基化合物与苯乙烯在引发剂作用下，将“茂后”催化剂通过 $\sigma$ 键连接到高分子链上形成高分子化的“茂后”烯烃聚合催化剂。

本发明的另一目的是提供一种高分子化的“茂后” $\alpha$ -双亚胺镍基催化剂在烯烃聚合，尤其在乙烯聚合中的应用。

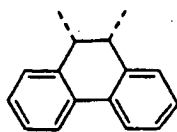
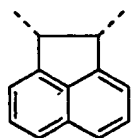
高分子化的“茂后” $\alpha$ -双亚胺镍基催化剂对烯烃聚合同样具有很高的催化活性，而且将“茂后”催化剂高分子化可以很容易地控制催化剂在分子链上的组成、分布，通过调节催化剂在分子链上的分布可以最大限度地发挥活性中心的催化作用。另外，高分子化“茂后” $\alpha$ -双亚胺镍基催化剂催化烯烃聚合所得到的聚合物不含无机灰分。

本发明制备的催化剂由 A 和 B 两组分组成，A 组分表达式为  $[P(S-co-Cat)]$  或  $[SiO_2-P(S-co-Cat)]$ ，P 表示共聚物，S 为聚苯乙

烯, *co* 表示共聚, Cat 表示 1-4 种含有烯烃基团的“茂后” $\alpha$ -双亚胺镍基催化剂。[P(S-*co*-Cat)] 是 1-4 种  $\alpha$ -双亚胺镍催化剂与苯乙烯的共聚物, 它具有如下结构:



其中 M 表示 Ni; X 为 Cl 或 Br; p 为 0-4 的整数; a、b、c、d、m、n、x 和 y 分别为 0-150 的整数;  $R_1$  与  $R_2$  可以相同或不同, 分别为 H、甲基、异丙基或叔丁基;  $R_3$  与  $R_4$  可以相同或不同, 分别为甲基、乙基、丙基或杂环, ET 是选自下述环状化合物的二价残基或其混合物:



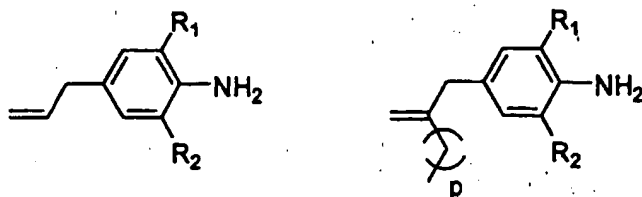
$SiO_2$  表示二氧化硅载体将高分子化催化剂 [P(S-*co*-Cat)] 固载化。B 组份为甲基铝氧烷或五氟苯硼 [ $B(C_6F_5)_3$ ] 其中任意一种。

催化剂的制备过程如下:

取代芳胺和烯烃基氯基或烯烃基溴生成的 N-烯烃基苯胺在无水氯

化锌存在下重排，得到 4-烯基芳胺，产率 25-71%。

其结构式为：

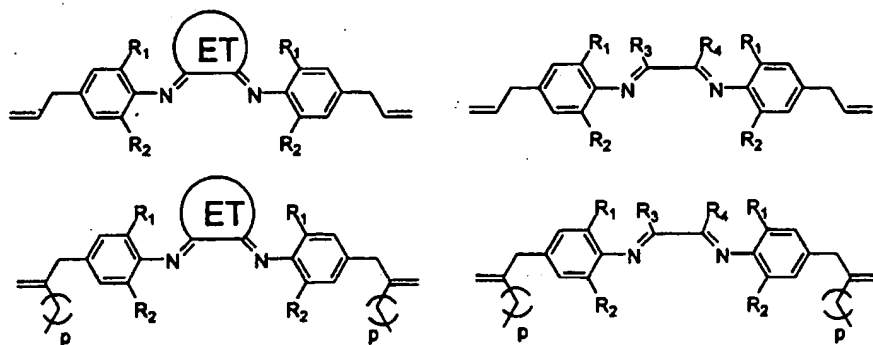


其中 R<sub>1</sub> 与 R<sub>2</sub> 可以相同或不同，分别为 H、甲基、异丙基或叔丁基，  
p 为 0-4 的整数。

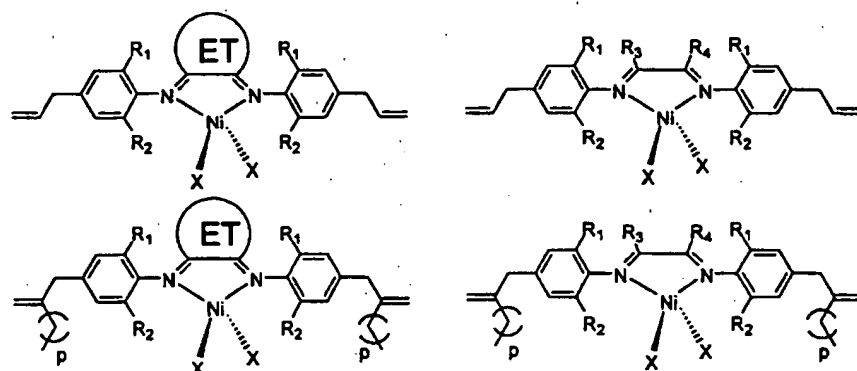
在甲酸、乙酸、CF<sub>3</sub>COOH 和盐酸的催化下，在酸和醇溶剂体系中与下式所示的 α-二酮进行缩合反应



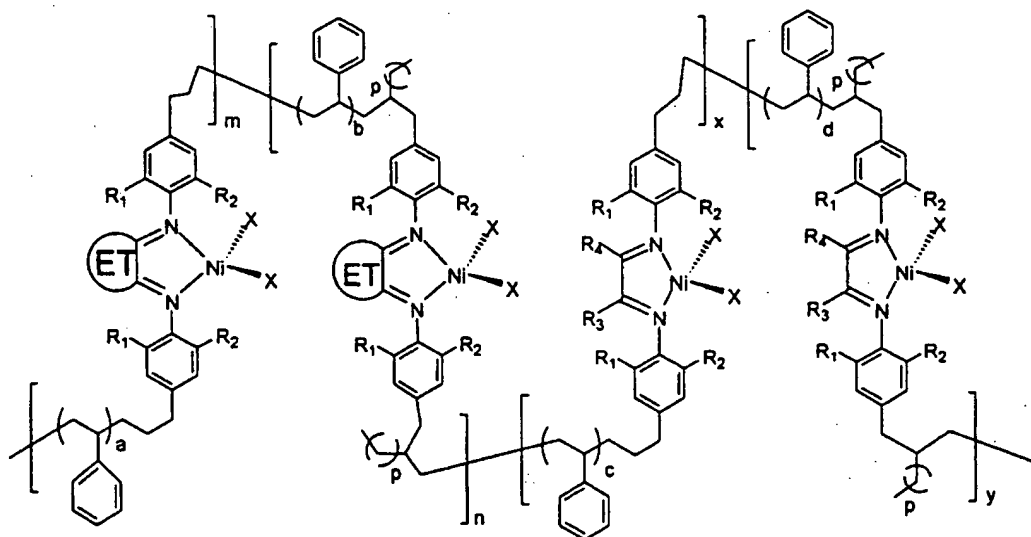
得到下式所示的含有烯基基团的 α-双亚胺配体，产率 72-84%；



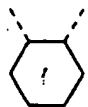
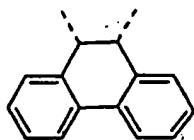
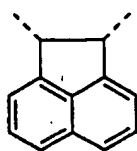
在无水无氧条件下，进行上述配体与 NiX<sub>2</sub>，其中 X 为 Cl 或 Br，的配位反应，得到下式含有烯基基团的 α-双亚胺 Ni(II) 配合物，产率 92-98%；



在无水无氧条件下，将含有烯烃基团的 $\alpha$ -双亚胺 Ni(II)配合物在 AIBN 引发下与苯乙烯共聚，使得催化剂通过  $\sigma$  键与聚乙烯链连结，得到如下式的高分子化“茂后”烯烃聚合催化剂：



其中 M 表示 Ni；X 为 Cl 或 Br；p 为 0-4 的整数；a、b、c、d、m、n、x 和 y 分别为 0-150 的整数； $R_1$  与  $R_2$  可以相同或不同，分别为 H、甲基、异丙基或叔丁基； $R_3$  与  $R_4$  可以相同或不同，分别为甲基、乙基、丙基或杂环，ET 是选自下述环状化合物的二价残基或其混合物：



$\text{SiO}_2$  表示二氧化硅载体将高分子化催化剂  $[\text{P}(\text{S-co-Cat})]$  固载化。

A 组分在助催化剂 B 组份, B 组份为甲基铝氧烷或五氟苯硼  $[\text{B}(\text{C}_6\text{F}_5)_3]$  的作用下, 在 1-20 个大气压下催化烯烃聚合, 活性数量级为  $10^5\text{--}10^7 \text{gPE}(\text{molNi}\cdot\text{h})^{-1}$ 。

具体实施方式如下:

#### 实施例 1: 烯丙基类芳胺的制备

将 2,6-二异丙基苯胺 0.2 摩尔和烯丙基氯 0.1 摩尔加热回流 8 小时, 冷却放置过夜, 倾入 400 毫升水中, 用氢氧化钠溶液碱化, 乙醚萃取, 真空减压蒸馏得 N-烯丙基-2,6-二异丙基苯胺 18.33 克, 产率为 84%。以 100 毫升甲苯为溶剂加入 N-烯丙基-2,6-二异丙基苯胺 0.084 摩尔和无水氯化锌 0.1 摩尔, 氩气气氛下回流 5 小时, 冷却后倾入氢氧化钠水溶液中碱化, 分离出有机层, 下层不溶物溶于热的浓盐酸中, 再倾入上述乙醚萃取液中, 无水硫酸镁干燥, 真空浓缩后减压蒸馏得 4-烯丙基-2,6-二异丙基苯胺 12.92 克, 产率为 71%。

#### 实施例 2: 烯丙基类芳胺的制备

将 2-特丁基苯胺 0.1 摩尔和 1-溴-2-丁烯基 0.05 摩尔加热回流 10 小时, 冷却放置过夜, 倾入 200 毫升水中, 用氢氧化钠溶液碱化, 乙醚萃取, 真空减压蒸馏得 N-(2-甲基丙基)-2-特丁基苯胺 5.35 克, 产率 53%。以 200 毫升甲苯为溶剂加入 N-(2-甲基丙基)-2-特丁基苯胺 0.2 摩尔和无水氯化锌 0.2 摩尔, 氩气气氛下回流 8 小时, 冷却后倾入氢氧

化钠水溶液中碱化, 分离出有机层, 下层不溶物溶于热的浓盐酸中, 再倾入上述乙醚萃取液中, 无水硫酸镁干燥, 真空浓缩后减压蒸馏得 4-(2-甲基丙烯基)-2-特丁基苯胺 24.89 克, 产率 61%。

### 实施例 3: 烯丙基类芳胺的制备

将 2,6-二甲基苯胺 0.12 摩尔和 1-溴-2-戊烯 0.06 摩尔加热回流 9 小时, 冷却放置过夜, 倾入 300 毫升水中, 用氢氧化钠溶液碱化, 乙醚萃取, 真空减压蒸馏得 N-(2-乙基丙烯基)-2,6-二甲基苯胺 3.72 克, 产率为 33%。以 80 毫升甲苯为溶剂加入 N-(2-乙基丙烯基)-2,6-二甲基苯胺 0.05 摩尔和无水氯化锌 0.05 摩尔, 氩气气氛下回流 7 小时, 冷却后倾入氢氧化钠水溶液中碱化, 分离出有机层, 下层不溶物溶于热的浓盐酸中, 再倾入上述乙醚萃取液中, 无水硫酸镁干燥, 真空浓缩后减压得 4-烯丙炔基-2,6-二甲基苯胺 2.77 克, 产率为 29%。

### 实施例 4: 烯丙基类芳胺的制备

将 2,6-二异丙基苯胺 0.1 摩尔和 1-溴-2-庚烯 0.05 摩尔加热回流 10 小时, 冷却放置过夜, 倾入 300 毫升水中, 用氢氧化钠溶液碱化, 乙醚萃取, 真空减压蒸馏得 N-(2-丁基丙烯基)-2,6-二异丙基苯胺 4.09 克, 产率为 30%。以 50 毫升甲苯为溶剂加入 N-(2-丁基丙烯基)-2,6-二异丙基苯胺 0.05 摩尔和无水氯化锌 0.05 摩尔, 氩气气氛下回流 8 小时, 冷却后倾入氢氧化钠水溶液中碱化, 分离出有机层, 下层不溶物溶于热的浓盐酸中, 再倾入上述乙醚萃取液中, 无水硫酸镁干燥, 真空浓缩后减压蒸馏得 4-(2-丁基烯丙基)-2,6-二异丙基苯胺 3.44 克, 产率为 25%。

### 实施例 5: 含有两个烯炔基团的双亚胺双齿配体的制备

2 毫摩尔  $\alpha$ -萘酮与 4 毫摩尔 4-烯丙基-2,6-二异丙基苯胺溶于 20 毫升乙酸中, 加热回流 1 小时后, 冷却到室温, 得到固体沉淀,



过滤，依此用乙酸洗涤（3×20 毫升）、正己烷洗涤（3×20 毫升），真空干燥，即得 $\alpha$ -双亚胺配体化合物  $C_{42}H_{48}N_2$  1.0 g，产率 84%。

#### 实施例 6：含有两个烯烃基团的双亚胺双齿配体的制备

3 毫摩尔 $\alpha$ -丁二酮与 6 毫摩尔 4-（2-甲基烯丙基）-2-特丁基苯胺溶于 30 毫升甲醇中，加 3-5 滴甲酸作催化剂，加热回流 1 小时后，冷却到室温，得到固体沉淀，过滤，依此用甲醇洗涤（3×20 毫升）、正己烷洗涤（3×20 毫升），真空干燥，即得 $\alpha$ -双亚胺配体化合物  $C_{36}H_{52}N_2$  1.2 g，产率 80%。

#### 实施例 7：含有两个烯烃基团的双亚胺双齿配体的制备

2.5 毫摩尔 $\alpha$ -环己二酮与 5 毫摩尔 4-烯丙基-2,6-二甲基苯胺溶于 25 毫升乙醇中，加 3-5 滴盐酸作催化剂，加热回流 1 小时后，冷却到室温，得到固体沉淀，过滤，依此用乙醇洗涤（3×20 毫升）、正己烷洗涤（3×20 毫升），真空干燥，即得 $\alpha$ -双亚胺配体化合物  $C_{28}H_{34}N_2$  1.0 g，产率 72%。

#### 实施例 8：含有两个烯烃基团的双亚胺双齿配体的制备

2.5 毫摩尔 $\alpha$ -菲二酮与 5 毫摩尔 4-（2-丁基烯丙基）-2,6-二异丙基苯胺溶于 30 毫升甲醇中，加热回流 1 小时后，冷却到室温，得到固体沉淀，过滤，依此用甲醇洗涤（3×20 毫升）、正己烷洗涤（3×20 毫升），真空干燥，即得 $\alpha$ -双亚胺配体化合物  $C_{52}H_{66}N_2$  1.5 g，产率 82%。

#### 实施例 9：含有两个烯烃基团的 $\alpha$ -双亚胺镍基催化剂的制备

催化剂的制备在无氧无水及高纯氩气保护条件下进行。以 30ml 二氯甲烷为溶剂，将实施例 5 中得到的二亚胺配体 1mmol 与 1mmol  $[Ni(DME)Br_2]$  (DME:二甲基乙二醚)在室温下搅拌 12 小时，真

空浓缩除去溶剂,用 50ml 乙醚洗涤沉淀 3-5 次,真空干燥,得 $\alpha$ -双亚胺镍基催化剂  $C_{42}H_{48}N_2NiBr_2$  0.8g, 产率 98%。

#### 实施例 10: 含有两个烯烃基团的 $\alpha$ -双亚胺镍基催化剂的制备

催化剂的制备在无氧无水及高纯氩气保护条件下进行。以 40ml 二氯甲烷为溶剂,将实施例 6 中得到的二亚胺配体 1mmol 与 1mmol  $[Ni(DME)Cl_2]$  (DME:二甲基乙二醚)在室温下搅拌 48 小时,真空浓缩除去溶剂,用 50ml 乙醚洗涤沉淀 3-5 次,真空干燥,得 $\alpha$ -双亚胺镍基催化剂  $C_{36}H_{52}N_2NiCl_2$  0.6g, 产率 98%。

#### 实施例 11: 含有两个烯烃基团的 $\alpha$ -双亚胺镍基催化剂的制备

催化剂的制备在无氧无水及高纯氩气保护条件下进行。以 30ml 二氯甲烷为溶剂,将实施例 7 中得到的二亚胺配体 0.5mmol 与 0.5mmol  $[Ni(DME)Br_2]$  (DME:二甲基乙二醚)在室温下搅拌 24 小时,真空浓缩除去溶剂,用 50ml 乙醚洗涤沉淀 3-5 次,真空干燥,得 $\alpha$ -双亚胺镍基催化剂  $C_{28}H_{34}N_2NiBr_2$  0.3g, 产率 96%。

#### 实施例 12: 含有两个烯烃基团的 $\alpha$ -双亚胺镍基催化剂的制备

催化剂的制备在无氧无水及高纯氩气保护条件下进行。以 40ml 二氯甲烷为溶剂,将实施例 8 中得到的二亚胺配体 1mmol 与 1mmol  $[Ni(DME)Cl_2]$  (DME:二甲基乙二醚)在室温下搅拌 72 小时,真空浓缩除去溶剂,用 50ml 乙醚洗涤沉淀 3-5 次,真空干燥,得 $\alpha$ -双亚胺镍基催化剂  $C_{42}H_{64}N_2NiCl_2$  0.7g, 产率 92%。

#### 实施例 13: 高分子化“茂后” $\alpha$ -双亚胺镍基催化剂 A 组分的制备

在无氧无水条件下,将实施例 9 中得到的含有烯烃基团的“茂后” $\alpha$ -双亚胺镍基催化剂  $C_{42}H_{48}N_2NiBr_2$  2mmol, 苯乙烯 5ml, 偶氮二